PATENT SPECIFICATION (11) 1324898

1324898

DRAWINGS ATTACHED

(21) Application No. 29077/71 (22) Filed 22 June 1971
(31) Convention Application No. 48961 (32) Filed 23 June 1970 in
(33) United States of America (US)
(44) Complete Specification published 25 July 1973
(51) International Classification B32B 5/28, 15/14, 17/04
(52) Index at acceptance
B5N 17Y 184 186 22Y 236 250 253X 308X 344 346 348 35Y 420 421 422 423 424 425 42X 430 43X 55Y 582 609 61Y 638 667 669 66X 66Y 67X 67Y 798

(19) THE PATENT OFFICE LONDON

(54) GRAPHITE-FIBER-REINFORCED LAMINATES

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindberg Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a graphite fiber reinforced laminar composite structure having high impact resistance.

Laminar composite structural materials are receiving increased recognition in industry, particularly in areas where high strength/high moduli, and low density materials are needed. With the advent of high tenacity, high modulus graphite fibers, many designs and types of graphite-fiber-reinforced laminar composite structures have been fabricated which upon first analysis appear to be ideally suited for use in turbine blades for jet aircraft, space vehicles, and the like, where high strength, high moduli and light weight materials are desired.

Unfortunately, graphite fiber reinforced structures, particularly in laminate form, have been found to be highly vulnerable to impact. Since the anticipated uses of graphite fiber reinforced laminates are in structures such as high speed aerospace vehicles and turbine blades, the impact sensitivity of these laminates casts serious doubts upon their applicability, notwithstanding their remarkable high strength/high moduli and low density characteristics. Thus, it is the primary object of the present invention to provide a reinforced graphite fiber laminar structure having improved resistance to impact.

The impact-resistance laminate of the invention is one of fibers set in a resin matrix, and comprising at least one layer of graphite fibers and at least one layer of elastic fibers having an elastic elongation to break equal to or greater than twice the elastic elongation to break of the graphite fibers, wherein at at least one surface of the laminate, the outermost layer of fibers is a layer of elastic fibers.

In accordance with one embodiment of the present invention, it has been found that bonding a layer which contains fibers having high resiliency and strength to one side of a graphite fiber laminar composite sharply improves the resistance to impacts occurring on the opposite side. It is thought that the additional layer positioned on the first side, sometimes herein referred to as the reverse impact side, provides a mechanism for dissipating the energy generated by impact away from the surface fibers of the graphite fiber layers located on the impact side of the laminate. The positioning of the layer is critical since it has been noted that arbitrary positioning of the additional layer may result in, at most, insignificant improvement in impact characteristics, particularly in the case of multi-layer laminates. Arbitrary positioning may result in the added layer being centered within the multilayer laminate, i.e., internally of the outermost graphite layer on the reverse impact side thereby adding little to the total impact resistance of the composite.

Accordingly, the invention also includes an article susceptible in use to impact from a given direction, the article being fabricated from a laminate of the invention arranged so that the outermost fiber layer on the opposite side of the laminate from the said direction is a layer of elastic fibers.

A laminate formed by bonding a layer of elastic fibers to one side of a graphite fiber laminate shows practically no improvement in resistance to impacts occurring on the elastic fiber layer. No advantages could therefore be predicted for placing an elastic fiber layer on the impact side of a graphite fiber/elastic fiber laminate already having an elastic fiber layer as the outermost fiber layer on the reverse impact side. Surprisingly, however, the

incorporation of two layers of elastic fibers, one on each side of the graphite fiber layer or layers, provides a synergistic increase in impact resistance, i.e. more than the combined total of impact resistance due to each acting singularly.

In preferred laminates of the invention, therefore, the outermost layer of fibers at each surface of the laminate is a layer of elastic fibers.

As used herein, the term fiber layer includes one or more plies in which the fibers are positioned unidirectionally. Thus, a fiber layer itself, on one extreme, may be unidirectional when all the component plies are oriented in the same direction and, on the other extreme, may be quasi-isotropic when the component plies are positioned so as to provide specific properties which are about the same in all directions. The latter may be visualized, for example, by imagining an eleven-ply fiber layer with each ply having a 15° orientation with respect to the adjacent ply or plies. The specific properties are about the same in all directions.

It has been found that it is preferable that the elastic fiber ply or plies contiguous to the graphite fiber layer have approximately the same orientation as the adjacent graphite fiber. In other words, at the elastic fiber-graphite fiber interface or interfaces, it is preferable that the fibers should have the same orientation. The orientation promotes optimum impact strength.

In order to retain to a significant extent the desirable physical characteristics for which the graphite fiber reinforcement is used, it is preferable in the laminates of the invention to limit the volume percent ratio of elastic fiber to a range of from 5 to 50% with optimum results occurring at from 5 to 30%.

The types of elastic fibers which may be utilized are varied. Many inorganic fibers such as, for example, S-glass and E-glass fibers can be used. Examples of organic fibers suitable for use are fibers made from high strength, high modulus aromatic polymers of the amide class such as described and claimed in U.S. Patent 3,232,910 and in *Journal of Polymer Science*, Part B, Vol. 5, pp 807, 812 (1967). Fibers having an elastic elongation to break as small as twice that of graphite fiber (about 0.5%) may be used as described herein. It is preferable, however, to employ fibers such as, for example, standard E-glass fibers which have an elongation to break of about 2.5% or about five times that of the graphite fiber.

Improved impact resistance may also be provided to graphite fiber reinforced laminates which include still other components. For example, the laminate may include one or more layers of metallic foil. The utilization of metallic foil with graphite fiber layers in a laminate demonstrates increased specific transverse modulus and strength in comparison to all-graphite fiber laminar composites. Like all-graphite fiber laminates, such laminates are not highly resistant to impacts normal to the surfaces. It has been found, however, that the incorporation of elastic fibers in the manner previously described significantly improves the impact resistance of the laminate.

In a fiber-reinforced laminate of the invention, the fibers are set in a resin matrix. The resin may be any of the thermosetting or thermoplastic resins that is compatible with graphite and the elastic fibers used, for example an epoxy resin.

Embodiments of the invention will now be described with reference to Figures 1, 2 and 3 of the accompanying drawings which illustrate in vertical cross-section various arrangements of laminates constructed in accordance with the present invention.

Figure 4 illustrates a typical test apparatus utilized to determine impact resistances of laminar composites.

The simplest embodiment, a laminate *10*, an arrangement of one layer 11 of elastic fibers and one layer of graphite fibers 12, is illustrated in Figure 1. The arrangement of Figure 1 depicts layer 12 with 3 plies of graphite fiber with an 0°, 0°, 90° fiber orientation adhered to a single-play layer 11 of elastic fibers with a 90° fiber orientation. Impact occurs on the opposite side from the elastic fiber layer 11. When compared to a 4-ply all-graphite fiber laminate (0°, 90°, 90°, 0°), a laminate as illustrated in Figure 1 demonstrates a marked improvement in impact resistance. On the other hand, when impacts occur directly against the elastic fiber layer, a laminar configuration such as that depicted in Figure 1 displays almost no increase in impact resistance.

Figure 2 illustrates a laminate *13* with a 3-ply layer 14 of graphite fiber (0°, 90°, 0°) sandwiched between layers 15 and 16 of elastic fiber (0°). The resistance to impacts occurring from either direction normal to the surfaces of laminate *13* is greater than the impact resistance of a 5-ply graphite fiber laminate with identical fiber orientation. More important, however, when compared to a similar all-graphite fiber laminate, the increase in impact resistance of laminate *13* is greater than the combined total of increase in impact resistance of 4-ply graphite fiber, single-ply elastic fiber laminate (reverse impact side) and the same with elastic fiber ply on the impact side.

Figure 3 illustrates a typical metal foil/graphite fiber laminate *16* with the graphite fiber layers 17 (90°, 0°, 90°) sandwiched between elastic fiber layers 18 (90°). Metal foil layers 19 are interleaved between the graphite fiber and elastic fiber layers.

Experimental tests for impact strength were conducted on a test apparatus as schematically illustrated in Figure 4. A dart 20 is positioned

a predetermined distance above a test specimen 21. Specimen 21 is supported by an open frame 22 which contacts specimen 21 around the edges thereof.

Dart 20 is released by an electrically operated trigger (not shown) which inactivates an electro-magnet 23 which secures dart 20 to stand 24. The height of the drop (a direct index of foot pounds energy) which results in initial failure on the reverse side of the sample is used as a measure of impact energy.

The following Examples are representative of experimental runs conducted on a number of test specimens. Examples 1—9 and 16 are comparative Examples. Initially a series of experimental tests was conducted on a plurality of all graphite fiber layer laminates. The laminates comprised HMG—50 (trade mark) graphite fiber (50×10^6 modulus, 300×10^3 psi tensile strength), a product of Hitco Co., 533 South Fremont Street, Los Angeles, California, U.S.A., in an epoxy matrix resin between about 55—60 volume percent fiber. All plies had unidirectional orientation. A testing apparatus similar to that depicted by Figure 4 was utilized. A steel dart weighing approximately 1.2 lbs and having a radius of curvature at the tip of about ⅜" was elevated above the specimen held in open frame support. The distance between the frame edges was approximately 2¾". Unless otherwise indicated, failure at the specified drop distance means failure by crack formation transverse to the graphite fibers. Table I illustrates the results attained for each graphite fiber laminate tested.

TABLE I

All Graphite Fiber Composites

Example	No. of Plies	Ply Orientation	Impact Drop Results
1	4	0°, 90°, 90°, 0°	Failure at 4"
2	7	0°, +60°, —60° 0°, −60°, +60°, 0°	Failure at 6"
3	5	0°, 90°, 0°, 90°, 0°	Failure at 4"
4	16	4 at ± 45° 8 at ± 0° 4 at ± 45°	Failure at 16"

The results of impact tests conducted on specimens as illustrated by Table I indicate that impact sensitivity of graphite fiber laminates is largely independent of fiber orientation and thickness. Failures occurred for relative short impact distances. In other experimental runs, it was found that impact sensitivity is also largely independent of the chemical composition of high modulus resins, fiber strength and modulus as represented by present commercial fibers.

A second set of experimental runs was conducted on graphite fiber-metal foil composites. The metal foils used were aluminum, titanium, and steel of various thickness as indicated in Table II. The graphite fiber was the same as used in the experimental runs shown in Table I.

TABLE II

Graphite Fiber/Metal Foil Composites

Example	Description	No. of Plies	Ply Orientation	Impact Drop Results
5	a) 2 mil steel b) graphite fiber	a) 2 b) 4 (S)[1]	a) — b) 0°, 90°, 90°, 0°	Failure at 8"
6	a) 5 mil aluminium b) graphite fiber	a) 5 b) 4 (I)[2]	a) — b) 0°, 90°, 90°, 0°	Failure at 8"
7	a) 5 mil aluminium b) graphite fiber	a) 11 b) 10 (I)	a) — b) all 0°	Failure at 12"
8	a) 2.6 mil titanium b) graphite fiber	a) 2 b) 4 (S)	a) — b) 0°, 90°, 90°, 0°	Failure at 4"
9	a) 2 mil aluminium b) graphite fiber	a) 4 b) 3 (I)	a) — b) 0°, 90°, 0°	Failure at 4"

[1] Used to signify that the metal foil layers sandwich the graphite fiber layer.
[2] Used to signify that the metal foil and graphite fiber layers are interleaved.

The significance of the results in Table II is that the use of isotropic materials such as metallic foils in graphite fiber composites does not increase the impact resistance of the composite.

The glass fiber layers in the graphite fiber/glass laminate structures as shown in Table III comprised E-glass fibers in an epoxy resin matrix. Each glass fiber ply had unidirectional orientation with approximately 55 to 60 volume percent fiber loading in each ply. The composition of the graphite fiber plies was identical to those of Table I.

The results of Table III take on increasing significance when compared to those of Table I. For example, test specimen of Example 10 having the identical number of plies for specimen of Example 1 did not fail at an impact distance four times greater than the failure distance of specimen of Example 1. The Example 4 specimen had 16 plies of graphite fiber yet failed upon impact before the specimen of Example 10.

The importance of placing the glass fiber layer on the reverse impact side is illustrated by comparing Examples 10 and 11. Glass fiber layers on the impact side appear to offer little help in resisting impact. This may be seen by comparing Examples 1 and 11.

TABLE III

Graphite Fiber/Glass Fiber Composites

Example	Description	No. of Plies	Ply Orientation	Impact Drop Results
10	a) glass fiber b) graphite fiber	a) 1 b) 3 glass ply on reverse side	a) 0° b) 90°, 90°, 0°	No failure at 16″
11	a) glass fiber b) graphite fiber	a) 1 b) 3 glass ply on impact side	a) 0° b) 90°, 90°, 0°	Failure at 6″
12	a) glass fiber b) grahite fiber	a) 2 (S)[1] b) 4	a) both 0° b) 90°, 0°, 0°, 90°	Failure at 32″
13	a) glass fiber b) graphite fiber	a) 2 (S)[1] b) 4	a) both 0° b) 0°, 90°, 90°, 0°	No failure at 32″
14	a) glass fiber b) graphite fiber	a) 8 (two 4-ply layers) (S)[1] b) 16	a) all 0° b) 8 at ± 45° 8 at 0°	Failure at 32″ with a 2.4 lb dart
15	a) glass fiber b) graphite fiber	a) 4 (S)[1] b) 4	a) 0° & 90° top, 90° & 90° bottom b) 90°, 0°, 0°, 90°	No damage at 32″
16	a) glass fiber b) graphite fiber	a) 4 (S)[2] b) 8 (two 4-ply layers)	a) 0°, 90°, 90°. 0° b) all at 0°	Failure at 12″

[1] Glass fiber layers sandwich the graphite layer.
[2] Graphite layers sandwich the glass layer

Example 16 further illustrates the criticality of glass fiber layer positioning. In Example 16, the graphite fiber layers sandwich the glass fiber layers. Failure occurred much earlier than the less thick laminate of Example 15. On the other hand, there is an unexpected increase in impact resistance, i.e., a synergistic effect, when the graphite layers are sandwiched between glass fiber layers. That is, because glass fiber layers on the impact side provide little increase in impact resistance, one would normally expect little increase in impact resistance when adding a second glass fiber layer to a composite which already has a glass fiber layer on the reverse impact side. Comparison of Example 12 to Example 10, however, aptly illustrates the surprising result. Another interesting result is seen when comparing Examples 12 and 13. In Example 12, the glass and graphite fiber plies forming the interface are at a 90° angle with respect to each other. In Example 13, the plies are oriented parallel. Failure occurred earlier in Example 12, thus indicating the preferability for the glass and graphite interface plies having essentially the same fiber orientation.

Table IV illustrates a sampling of another set of experimental runs conducted on metal foil/glass fibre/graphite fiber laminar composites. The materials utilized were the same as those employed for Table II for the metal foil/graphite fiber and Table III for the glass fiber/graphite fiber composites.

TABLE IV

Graphite Fiber/Glass Fiber/Metal Foil Composites

Example	Description	No. of Plies	Ply Orientation	Impact Drop Results
17	a) graphite fiber b) 2 mil aluminum c) glass fiber	3 4 (I)[1] 4 all on reverse impact side	0°, 90°, 0° — 0°, 90°, 90°, 0°	No Failure at 16″
18	a) graphite fiber b) 2 mil steel c) glass fiber	4 7 (I)[2] 2 (S)[3]	0°, 90°, 90°, 0° — 0° top & bottom	No Failure at 32″
19	a) graphite fiber b) 2.65 mil titanium c) glass fiber	4 7 (I)[2] 2 (S)[3]	0°, 90°, 90°, 0° — 0° top & bottom	No Failure at 10″
20	a) graphite fiber b) 5 mil aluminum c) glass fiber	4 9 (I)[2] 4 (S) two 2-ply layers	90°, 0°,0°,90° — 0°, 0° top & bottom	No damage at 32″

[1] Metal foil interleaves the graphite layers.
[2] Metal foil interleaves both glass and graphite fiberlayers
[3] Glass layers sandwich graphite fiber layers

As is evident from a comparison of Tables IV and II, the positioning of glass fiber layer on the reverse impact side of metal foil/graphite fiber/glass fiber composite provides a marked increase in impact resistance.

In conclusion, the laminar composite of the present invention has, in its simplest arrangement, a layer of elastic fibers external of all of the graphite fiber layers on the reverse impact side. In another arrangement, the graphite fiber layers are sandwiched between elastic fiber layers which provide a synergistic increase in impact resistance. It is to be understood, however, that other elastic fiber layers and/or other components such as, for example, metallic foils, may be internal of some graphite layers to the extent that the presence thereof is not deleterious to the impact resistance increase and other required physical parameters. By way of example, it has been noted that up to 25% of the volume percent ratio of glass fiber present in a glass fiber/graphite laminate may be incorporated internally of some of the graphite layers without being detrimental to the impact resistance of the laminate.

WHAT WE CLAIM IS:—

1. An impact-resistant laminate of fibres set in a resin matrix, and comprising at least one layer of graphite fibres and at least one layer of elastic fibers having an elastic elongation to break equal to or greater than twice the elastic elongation to break of the graphite fibers, wherein at at least one surface of the laminate, the outermost layer of fibers is a layer of elastic fibers.

2. A laminate according to Claim 1, wherein the outermost layer of fibers at each surface of the laminate is a layer of elastic fibers.

3. A laminate according to either of Claims 1 and 2, wherein the elastic fibers are glass fibers.

4. A laminate according to any of Claims 1 to 3, wherein the elastic fiber layers constitute from 5 to 50% by volume of the laminate.

5. A laminate according to any of Claims 1 to 4, wherein at the interface between a graphite fiber layer and an elastic fiber layer the fiber orientation in each layer is the same.

6. A laminate according to any of Claims 1 to 5, wherein at least the elastic fiber layers each contain at least two plies having different fiber orientation.

7. A laminate according to any of Claims 1 to 6 including at least one layer of metallic foil.

8. A laminate according to Claim 7 having a metallic foil as a surface layer of the laminate, provided that in a laminate wherein metallic foil is the surface layer on one side, the outermost layer on the opposite side is a layer of elastic fibers.

9. A laminate according to Claim 7 having a metallic foil as the surface layer on both sides of the laminate.

10. A laminate according to Claim 1 substantially as described with reference to the accompanying drawings.

11. A laminate according to Claim 1 substantially as described in any of Examples 10, 12 to 15 and 17 to 20.

12. An article susceptible in use to impact from a given direction, the article being fabricated from a laminate according to any of Claims 1 to 11 arranged so that the outermost fiber layer on the opposite side of the laminate from the said direction is a layer of elastic fibers.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

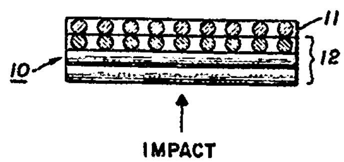

FIG. 1.

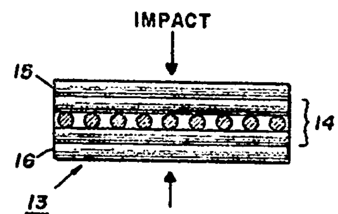

FIG. 2.

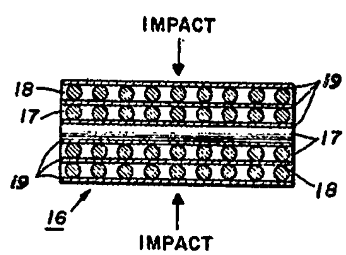

FIG. 3.

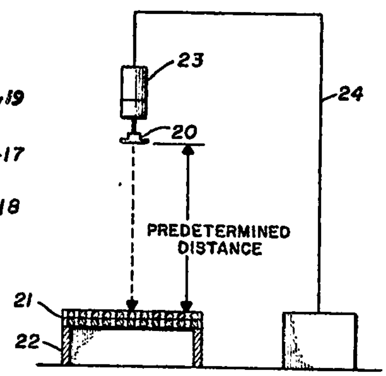

FIG. 4.